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# Structure of 1-cyano, 1-carbethoxy-2-(3' methoxy-4'-hydroxy) phenyl ethylene

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**Abstract** The title compound [$C_{11}H_{11}O_4N$] has been taken up for study as it shows non linear optical (NLO) properties with an electron withdrawing group at one end and an electron donating group at the other, with an extended conjugation in between. The crystal structure has been determined at room temperature. Needle like crystals of the compound crystallizes in monoclinic system, space group $P2_1/n$ with cell dimensions $a$ = 10.646(3)Å, $b$ = 9.351(4)Å, $c$ = 12.647(5)Å, $\beta$ = 97.13(3)° and $Z$ = 4. The structure was solved by direct method and refined by full-matrix least-squares method to a final $R$ = 0.046 for 1993 observed reflections. The molecule on the whole is almost planar, the methoxy group makes a dihedral angle of 0.7° with planar phenyl ring. The carbethoxy moiety forms an extended planar zigzag chain with the neighboring atoms. The molecules are held by strong O-H...O, C-H...O and C-H...N inter- and intra- molecular hydrogen bonds.

**Keywords** Phenyl ethylene, X-ray crystallography

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Non-centrosymmetric aromatic compounds like 4-nitro-2-methyl aniline have been found useful to study their nonlinear optical [NLO] studies[1], 4-arylidene pyridenes with hydroxyl groups have also been reported as possible nonlinear optical materials. During the present investigation, the compound as a push-pull molecule with electron donating -OH and -$OCH_3$ groups of the phenyl ring and a two armed conjugated side chain possessing cyano(CN) and ester groups as electron withdrawing groups conjugated with arylidene moiety expected to exhibit NLO properties of Secondary Harmonic Generators (SHG) activity. In order to ascertain the stereochemical relationship of cyano and carbethoxy groups attached to C1 with the aromatic moiety of C2 and to discuss the role of O-H...O interaction in stabilizing the packing mode, the crystal structure of the title compound has been studied.

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The title compound was obtained by the reaction of vanillin with ethyl cyanacetate using piperidene as catalyst. Equimolar quantities of the reactants were allowed to stand at ice bath temperature for three hours in presence of catalytic quantities of piperidene. The reaction mixture was worked up according to the literature method[2] and crystallized by slow evaporation technique using ethanol as solvent.

Intensity data were measured on Enraf-Nonius CAD4 diffractometer[3] with graphite-monochromatised, Mo$K_\alpha$ radiation, ($\lambda$ = 0.7107Å). The data was corrected for Lorentz and polarization factor[4]. The crystal data of the compound is given in Table 1. The structure was solved by direct method and refined by full-matrix least-squares method using SHELXL-97[5] program. Non-H atoms were refined with anisotropic thermal parameters. All hydrogen atoms have been geometrically fixed and refined for isotropic thermal parameters.

**Table 1.** Crystal data for the title compound

| | |
|---|---|
| Crystal morphology | Pale yellow, needle like |
| Chemical formula | $C_{11}H_{13}O_4N$ |
| Molecular weight | 247.24 |
| Crystal system | $P21/n$ |
| Space group | monoclinic |
| Cell constants | $a$ = 10.646(3)Å, |
| | $b$ = 9.351(4)Å, |
| | $c$ = 12.647(5)Å |
| | $\beta$ = 97.13(3)° |
| Volume | 1249.2(8) Å$^3$ |
| Number of formula unit Z | 4 |
| Density (calculated) $D_c$ | 1.315 gm/cc |
| Density (measured) $D_m$ | 1.297 gm/cc |
| Absorption coefficient $\mu(MoK_\alpha)$ | 0.098 mm$^{-1}$ |
| Unique data measured | 2447 |
| Observed data with $F0 > 4\sigma(F0)$ | 1993 |
| $F(000)$ | 520.00 |
| $R$ | 0.046 |
| $Rw$ | 0.108 |

The final positional and equivalent isotropic thermal parameters of non-hydrogen atoms are listed in Table 2. The anisotropic temperature factor for non-H atoms are presented in Table 3. The bond lengths, bond angles and torsion angles are given in Table 4. The chemical diagram of the molecule is as shown in Figure 1. An ORTEP[6] plot of the molecule with 30% probability thermal ellipsoids, viewed down $a$-axis is shown in Figure 2.

**Table 2.** The final positional and equivalent isotropic thermal parameters(Å$^2$) of non-hydrogen atoms with Estimated Standard Deviations (e.s.d's) in parentheses

| Atom | x | y | z | $U_{iso}$ |
|---|---|---|---|---|
| O1 | -0.2567(3) | -0.5462(3) | 1.0647(2) | 0.0794 |
| O2 | -0.0824(2) | -0.4130(3) | 1.2009(2) | 0.0747 |
| O3 | 0.1779(2) | 0.0477(3) | 0.7753(2) | 0.0759 |
| O4 | 0.3157(2) | 0.0988(3) | 0.9198(2) | 0.0[illegible] |
| N1 | 0.2434(3) | -0.0658(4) | 1.1386(3) | 0.1001 |
| C1 | 0.1545(3) | -0.0640(3) | 0.9401(2) | 0.0634 |
| C2 | 0.0546(3) | -0.1432(4) | 0.8990(2) | 0.0629 |
| C3 | 0.2055(3) | -0.0646(4) | 1.0506(3) | 0.0728 |
| C4 | 0.2156(3) | 0.0327(3) | 0.8682(2) | 0.0612 |
| C5 | 0.3807(4) | 0.2010(5) | 0.8582(3) | 0.0760 |
| C6 | 0.4796(4) | 0.2731(6) | 0.9319(4) | 0.0916 |
| C7 | 0.0100(4) | -0.3452(6) | 1.2751(3) | 0.0856 |
| C1' | -0.0234(3) | -0.2457(3) | 0.9468(2) | 0.0609 |
| C2' | -0.0097(3) | -0.2776(4) | 1.0562(2) | 0.0626 |
| C3' | -0.0872(3) | -0.3764(3) | 1.0961(2) | 0.0604 |
| C4' | -0.1804(3) | -0.4481(3) | 1.0277(3) | 0.0645 |
| C5' | 0.1937(3) | -0.4173(4) | 0.9201(3) | 0.0717 |
| C6' | -0.1165(3) | -0.3177(4) | 0.8799(3) | 0.0685 |

**Table 3.** Anisotropic temperature factor(Å$^2$) for non-hydrogen atoms with e.s.d's in parentheses

| Atom | $U11$ | $U22$ | $U33$ | $U23$ | $U13$ | $U12$ |
|---|---|---|---|---|---|---|
| O1 | 0.0840(2) | 0.0862(2) | 0.0703(2) | -0.0068(1) | 0.0183(1) | -0.0186(1) |
| O2 | 0.0810(2) | 0.0852(2) | 0.0579(1) | 0.0069(1) | 0.0087(1) | -0.0130(1) |
| O3 | 0.0794(1) | 0.0866(2) | 0.0585(1) | 0.0060(1) | 0.0195(1) | 0.0001(1) |
| O4 | 0.0720(1) | 0.0804(2) | 0.0677(1) | 0.0080(1) | 0.0148(1) | -0.0066(1) |
| N1 | 0.0980(2) | 0.1250(3) | 0.0717(2) | 0.0205(2) | -0.0161(2) | -0.0290(2) |
| C1 | 0.0616(2) | 0.0675(2) | 0.0599(2) | 0.0014(1) | 0.0149(1) | 0.0093(1) |
| C2 | 0.0665(2) | 0.0711(2) | 0.0525(2) | -0.0006(1) | 0.0138(1) | 0.0094(2) |
| C3 | 0.0643(2) | 0.0810(2) | 0.0720(2) | 0.0112(2) | 0.0059(2) | -0.0075(2) |
| C4 | 0.0649(2) | 0.0685(2) | 0.0618(2) | 0.0009(1) | 0.0185(1) | 0.0064(1) |
| C5 | 0.0770(2) | 0.0820(2) | 0.0750(2) | 0.0000(2) | 0.0238(2) | -0.0052(2) |
| C6 | 0.0780(3) | 0.1000(3) | 0.0970(3) | 0.0050(3) | 0.0170(2) | -0.0120(2) |
| C7 | 0.0900(3) | 0.0960(3) | 0.0601(2) | 0.0097(2) | -0.0001(2) | -0.0050(2) |
| C1' | 0.0618(2) | 0.0654(2) | 0.0568(2) | -0.0001(1) | 0.0120(1) | 0.0057(1) |
| C2' | 0.0630(2) | 0.0655(2) | 0.0587(2) | -0.0043(1) | 0.0053(1) | -0.0002(1) |
| C3' | 0.0610(2) | 0.0652(2) | 0.0575(2) | -0.0005(1) | 0.0125(1) | 0.0084(1) |
| C4' | 0.0629(2) | 0.0658(2) | 0.0675(2) | -0.0073(1) | 0.0156(1) | -0.0009(1) |
| C5' | 0.0686(2) | 0.0840(2) | 0.0619(2) | -0.0117(2) | 0.0085(2) | -0.0053(2) |
| C6' | 0.0713(2) | 0.0810(2) | 0.0526(2) | -0.0045(1) | 0.0093(1) | 0.0017(2) |

Table 4. Bond length (Å), bond angle (°) and torsion angle (°)for non-hydrogen atoms with e s.d?s in parentheses

| | | |
|---|---|---|
| **Bond lengths** | | |
| O1-C4' 1.347(4) | O2-C3' 1.363(4) | O2-C7 1.422(5) |
| O3-C4 1.202(4) | O4-C4 1.330(4) | O4-C5 1.461(4) |
| N1-C3 1.136(4) | C1-C2 1.346(5) | C1-C3 1.435(5) |
| C1-C4 1.489(4) | C2-C1' 1.448(4) | C5-C6 1.479(6) |
| C1'-C6' 1.394(4) | C1'-C2' 1.406(4) | C2'-C3' 1.376(4) |
| C3'-C4' 1.403(4) | C4'-C5' 1.381(4) | C5'-C6' 1.380(5) |

| | | | |
|---|---|---|---|
| **Bond angles** | | | |
| C3'-O2-C7 | 118.0(3) | C4-O4-C5 | 116.5(3) |
| C2-C1-C3 | 124.0(3) | C2-C1-C4 | 118.9(3) |
| C3-C1-C4 | 117.1(3) | C1-C2-C1' | 132.0(3) |
| N1-C3-C1 | 178.6(4) | O3-C4-O4 | 125.1(3) |
| O3-C4-C1 | 123.3(3) | O4-C4-C1 | 111.5(3) |
| O4-C5-C6 | 108.0(3) | C6'-C1'-C2' | 118.3(3) |
| C6'-C1'-C2 | 117.9(3) | C2'-C1'-C2 | 123.8(3) |
| C3'-C2'-C1' | 120.7(3) | O2-C3'-C2' | 125.0(3) |
| O2-C3'-C4' | 114.7(3) | C2'-C3'-C4' | 120.3(3) |
| O1-C4'-C5' | 119.4(3) | O1-C4'-C3' | 121.5(3) |
| C5'-C4'-C3' | 119.1(3) | C6'-C5'-C4' | 120.7(3) |
| C5'-C6'-C1' | 120.9(3) | | |

| | |
|---|---|
| **Torsion angles** | |
| C7-O2-C3'-C2' | - 0.4(5) |
| C1-C2-C1'-C2' | 3.4(5) |
| C3-C1-C2-C1' | - 1.5(6) |
| C4-O4-C5-C6 | 174.1(3) |
| C2-C1-C4-O3 | 2.5(5) |
| C5-O4-C4-O3 | 2.4(5) |

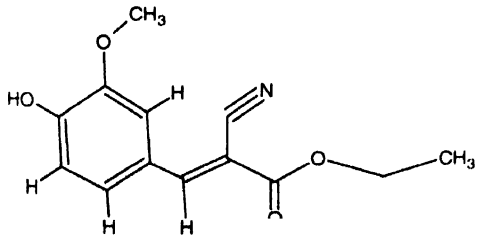


Figure 1. Chemical diagram of the molecule.

The phenyl ring is planar with O1 and C2 atoms lying in the least square planes while O2 and C7 lying below the plane by 0.016(3)° and 0.015(5)° respectively. The bond lengths and bond angles in the phenyl ring are normal. The methoxy group at C3' is coplanar with the phenyl ring. The torsion angle C7-O2-C3'-C2' is -0.4(5)°. The angle C2'-C3'-O2 is larger than the angle C4'-C3'-O2 by about 10°. This might be due to *cis* orientation of the O2-C7 bond and C2'-C3' bond about C3'-O2 bond which causes repulsion between the atoms C2' and C7 [7].

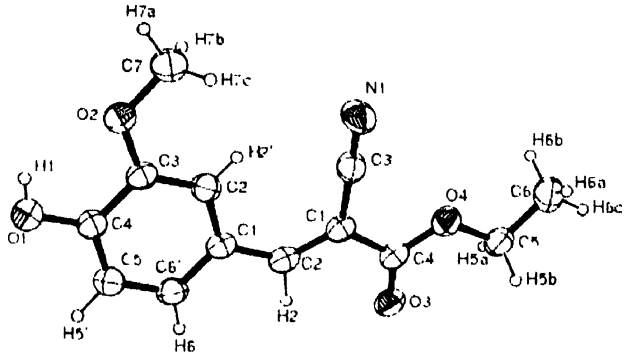


Figure 2. ORTEP plot of the molecule with 30% probability ellipsoids viewed down *a*-axis

The two armed conjugated side chain posses a linear C-C = N[C1 – C3 = N1 = 178.6(4)°] chain and zig zag ester groups. The bonds C4-O3=1.202(4)Å and C3-N1 = 1.136(5)Å show distinct double and triple bond character respectively. The conformation of $CH(CN)COOC_2H_5$ can be described by the torsion angles C1-C2-C1'-C2' is 3.4(5) and C3-C1-C2-C1' is 1.5(6). The torsion angle C4-O4-C5-C6=174.1(3) indicates anti-peri planar relation between the carbonyl carbon and the methyl group. The mean planes of the ethyl carbonate group makes dihedral angle of 6.30(1)° with the mean plane of phenyl ring. The torsion angle C2-C1-C4-O3 is 2.5(5)°. The C = O bond is *syn* to the ester group about the C-O, the torsion angle C5-O4-C4-O3 is 2.4(5)°.

The molecular packing of the molecule along *b*-axis is shown in Figure 3. The molecules are stabilized by intra- and inter-molecular hydrogen bondings. The oxygen atom O3 of the ester group makes a strong intra- molecular contacts while the hydrogen atom of the OH group at C4' gives a strong inter- and intra- molecular hydrogen bondings. The hydrogen bondings are listed in Table 5.

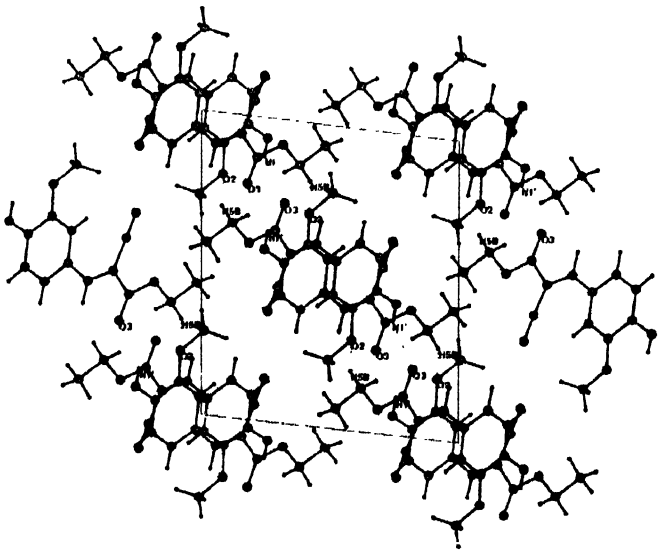

Figure 3. Packing diagram of the molecule viewed along *b*-axis

**Table 5.** Hydrogen bondings (Å, °)

| D-H . .A | D-H | H . A | D | D-H A |
|---|---|---|---|---|
| O1-H1' . .. O2' | 0 751(47) | 2 230(44) | 2 678(04) | 119 21(43) |
| C2-H2 O3' | 0 977(32) | 2 404(32) | 2.804(04) | 103 89(22) |
| C2'-H2' .. N1' | 0.885(28) | 2.598(29) | 3 402(05) | 151 39(25) |
| O1-H1' . .. O3'' | 0 751(47) | 2 179(50) | 2 835(04) | 146 38(47) |
| C5-H5B .. O2''' | 0 975(43) | 2 563(42) | 3 399(05) | 143 83(32) |

Equivalent positions

(i) x, y, z

(ii) $x - 1/2, -y - 1/2, +z + 1/2$

(iii) $x + 1/2, -y - 1/2, +z - 1/2$

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